

The diagram shows a cross-sectional view of a semiconductor device. It includes a substrate (7) with a top layer (82). Below the top layer are several regions labeled 5, 2-2, 3, 2-1, and 4. A central rectangular region is labeled 9. To the right of this region is another area labeled 12. Electrical contacts are shown at the top: one labeled 14 with a '+' sign, and another labeled 81 with a '-' sign. A dashed line indicates a connection path from the central region (9) through a contact (13) to a component labeled 101. Another dashed line connects the right side (12) through a contact (112) to a component labeled 102.

LIQUID FUEL CELL

1 BACKGROUND OF THE INVENTION

This invention relates to a liquid fuel cell, and particularly to a liquid fuel cell capable of stable operation for a prolonged time under controlled supply of
5 fuel and water.

Generally, fuel cells using a liquid fuel are classified into an acid type and an alkali type, and methanol, formalin, hydrazine, etc. are used as fuel. The working principle of such fuel cells will be briefly
10 described, referring to Fig. 1, where numeral 1 shows a fuel cell and symbols + and - show terminals for outputting electricity. The fuel cell 1 comprises a fuel electrode 2-1, an oxidizing agent electrode 2-2 counterposed to the fuel electrode 2-1 (the oxidizing agent electrode can be
15 called "oxygen electrode" when oxygen is used as an oxidizing agent, or "air electrode" when air is used as an oxidizing agent), an electrolyte chamber provided between the oxidizing agent electrode 2-2 and the fuel electrode 2-1, a fuel chamber 4 provided adjacent to the fuel
20 electrode 2-1, and an oxidizing agent chamber 5 provided adjacent to the oxidizing agent electrode 2-2. In Fig. 1, numeral 6 shows the fuel (which may contain water), or a mixture of fuel and electrolyte and also shows its flow direction, and numeral 7 likewise shows the oxidizing agent
25 and also shows its flow direction.

1 The fuel cell as structured above works as
follows. When the fuel 6 is supplied to the fuel chamber
4 and when the oxidizing agent 7 is supplied to the
oxidizing chamber 5, the fuel 6 permeates into the fuel
5 electrode 2-1 to generate electrons through the electro-
chemical reaction. When a load is given to the external
circuit, a direct current can be obtained. In this case,
a product 81 is formed in the fuel chamber 4. The product
is a carbon dioxide gas or carbonate when the fuel is
10 methanol, formic acid or formalin, and nitrogen when the fuel
is hydrazine. When the supply of fuel 6 of a circulating
type, the product contains excess fuel or electrolyte, and
it is necessary to separate and vent the gaseous product
from the circulation system.

15 On the other hand, when the oxidizing agent 7 is
supplied to the oxidizing agent chamber 5, the oxidizing
agent 7 permeates and diffuses into the oxidizing agent
electrode 2-2 to consume electrons through the electro-
chemical reaction. When the electrolyte is of an acid type,
20 a product 82 is formed. The product is mainly water and
contains excess air. When the electrolyte is of a base type,
water is formed at the fuel electrode 2-1.

 When an aqueous solution of electrolyte such as
sulfuric acid or potassium hydroxide is used in the
25 electrolyte chamber 3 in the unit fuel cell 1 structured as
in Fig. 1, the aqueous solution leaks from the electrolyte
chamber 3 and thoroughly permeates also into the electrodes,
and a good cell performance can be obtained. However, the

1 aqueous solution of electrolyte also leaks into the fuel
chamber 4 in this case, and thus it is necessary to supply
fuel mixture containing the aqueous solution of electrolyte
prepared in advance as anolyte. To this end, the fuel
5 chamber 4 is provided with a circulation system for supply-
ing the fuel mixture to the fuel chamber 4 by a pump 9 and
a system for supplying the fuel from a fuel tank 10 through
a valve 11 to the circulation system, as shown in Fig. 2.

It has been also proposed to use an aqueous
10 solution of polymeric electrolyte in the electrolyte
chamber 3 in place of the acid electrolyte, and provide the
fuel chamber with a circulation system for a fuel mixture
of fuel and water adjusted to a most suitable concentra-
tion for the operation as in Fig. 2, and also with a system
15 for supplying the fuel from the fuel tank 10 to the
circulation system.

As shown in Fig. 2, the product gas 811 is vented
from the circulation system after the passage through the
fuel chamber 4, and the remaining mixture 812 is recycled
20 to the fuel chamber.

According to the conventional fuel supply system
as described above, a fuel mixture in a constant mixing
ratio prepared in advance is supplied to the circulating
system from the single fuel tank 10 shown in Fig. 2.
25 However, it has been found that the consumption ratios of
fuel and water in the circulation mixture 6 containing the
fuel are not always constant, and depend on changes in load,
changes in temperature of fuel cell during the operation,

1 even though the load is constant, or changes in flow rate and
temperature or humidity of the air supplied as the oxidizing
agent.

In a fuel cell using a liquid fuel, the fuel
5 supply system contains two essential components, i.e. fuel
and water, and further may contain an electrolyte. In the
most cases, these three components, i.e. fuel, water and
electrolyte are usually contained in the fuel supply system.
Among these three components, it is the fuel and water that
10 are consumed. Usually, it is not necessary to take
consumption of electrolyte into consideration. Consumption
rate of fuel differs from that of water, because firstly
water is always consumed at one electrode, whereas at
another electrode water is always formed as a result of the
15 electromotive reaction of a fuel cell, and formation of
water at the fuel electrode or the oxidizing agent electrode,
depends on the acidity or the alkalinity of electrolyte.
That is, in the case of an acidic electrolyte, water is
formed at the oxidizing agent electrode and consumed at the
20 fuel electrode, whereas in the case of an alkaline
electrolyte, the formation and consumption of water are
reversed. In that case, one mole or two moles of water is
principally formed with one mole of fuel throughout the
reaction, depending on the species of fuel. Since the
25 consumption and formation of water take place at the
different electrodes, water actually tends to migrate
through the electrolyte chamber to keep a water balance.
Even in view of this tendency, water is short at one

1 electrode and in excess at another electrode, owing to much
dissipation of water and difficulty to keep the water
balance well throughout the electrolyte chamber.

Secondly, the excess or shortage of water due to
5 water imbalance in the water migration between the
electrodes largely depends on the operating temperature and
the load current.

Thirdly, the excess fuel that is not converted to
the electric current at the fuel electrode migrates through
10 the electrolyte chamber and permeates into the oxidizing
agent electrode to occasion direct oxidation of the fuel,
or water migrates as hydronium ions when the electrolyte
ions migrate in the electrolyte chamber in the case of an
acidic electrolyte. These phenomena also depend on the
15 load current and operating temperature of a fuel cell.
Furthermore, the amount of water carried by the oxidizing
agent, for example, air by evaporation at the oxidizing
agent electrode side depends on the feed rate, temperature
and humidity of the oxidizing agent.

20 The consumption rate of fuel differs from that
of water on the grounds as described above, and thus the
supply of a mixture of fuel and water only in a constant
mixing ratio from a single tank to the fuel circulation
system as shown in Fig. 2 can only meet a change in the
25 amount of only one component among the two components, i.e.
fuel and water, in the fuel circulation system including
the fuel chamber. That is, adequate control over the fuel
and water cannot be made, and stable and prolonged operation

1 of a fuel cell is quite impossible to conduct. That is,
the fuel in the fuel circulation system may be so
concentrated that the heat is much generated or the current
output is lowered, or the supply of fuel fails to catch
5 up with the consumption, so that the fuel becomes short
in the fuel circulation system.

In a fuel cell using a liquid fuel, the cell
voltage V shows a flat peak in a certain range of concent-
ration C_m of fuel 6 when the current is constant. At a
10 lower fuel concentration C_m , the fuel becomes short and
the cell voltage is lowered, whereas at a higher fuel
concentration C_m , the excess fuel that fails to take part
in the reaction at the fuel electrode 2-1 migrates through
the electrolyte chamber 3 and permeates into the oxidizing
15 agent electrode 2-2 to occasion direct combustion of fuel.
As a result, the potential on the oxidizing agent electrode
2-2 is lowered with generation of heat, and consequently
the cell voltage is lowered. When the fuel concentration
is too high or too low (e.g. less than C_{m1} or more than C_{m2}
20 in Fig. 3), the ratio of the necessary amount of electrical
energy-converted fuel to the amount of consumed fuel will
be lowered, and thus the fuel utilization efficiency is
considerably lowered. Thus, it is very important to select
an appropriate fuel concentration.

25 An appropriate range of the fuel concentration,
i.e. the range of fuel concentration, C_{m1} to C_{m2} , shown in
Fig. 3, has been so far experimentally studied by many
researchers. For example, in the case of an acidic

1 electrolyte type fuel cell using methanol as fuel, it is
disclosed in 24th Cell Panel Discussion Lectures No. 2B02,
page 254 that the concentration C_{m1} is 0.5 moles/l and the
concentration C_{m2} is 2 moles/l at the current density of
5 64 mA/cm². Japanese Patent Application Kokai (Laid-open)
No. 56-118273 discloses that the concentration C_{m2} is
about 5% by weight (about 1.6 moles/l).

On the other hand, even in a liquid fuel cell
using hydrazine as fuel, Japanese Patent Publication No.
10 48-31300 discloses that stable operation is possible at
1.5% by weight (0.5 moles/l), and if the concentration is
less than 1.5% by weight, the voltage is lowered and the
temperature is increased.

It is seen from the foregoing that the fuel
15 concentration range for stable operation is about 0.3
moles/l as C_{m1} and about 2 moles/l as C_{m2} .

Thus, the fuel concentration is very important
in the fuel cell, and a more accurate apparatus for detecting
or measuring the fuel concentration is still required.

20 A liquid fuel cell provided with an apparatus for
detecting a fuel concentration now in practical use is
shown in Fig. 4, where the same members as in Fig. 1 and
Fig. 2 are indicated with the same reference numerals.

An oxidizing agent 7 is supplied to an oxidizing
25 agent chamber 5 by a blower 111, and discharged as a
residual gas 82. On the other hand, a fuel supply system
includes a system for circulating a mixture of fuel and an
electrolyte solution (the mixture may be called "anolyte")

1 by a pump 9 and a system for supplying an appropriate
amount of fuel to an anolyte tank 20 provided in the
circulation system from a fuel tank 10 through a valve 17.
The circulation system is open to the outside at an
5 appropriate position to discharge the product gas 811.

The fuel is supplied by opening the valve 17, and
the opening or closure or control of the valve 17 is made
by an apparatus 13 for detecting a fuel concentration
provided in the anolyte tank 20 and a valve controller 171.

10 The apparatus 13 for detecting a fuel concentra-
tion comprises an anode electrode 517 (which will be herein-
after referred to merely as "anode"), a cathode electrode
518 counterposed to the anode (the cathode electrode will
be hereinafter referred to merely as "cathode"), a power
15 source 519, and a detector 520. The anode 517 comprises a
platinum plate 517a and a membrane 517b tightly laid on the
platinum plate 517a by pressing.

With such a structure as described above, when a
DC voltage of e.g. 0.85 V is applied to between the anode
20 517 and the cathode 518, the quantity of electric current
changes proportionally to the methanol concentration in the
anolyte. Thus, it is possible to determine the concentra-
tion of methanol as fuel in a very simple structure.

However, the concentration of methanol can be
25 indeed determined by the apparatus with such a structure
as described above, but its detection sensitivity is not
better, as given below.

Relationship between the fuel concentration and

1 detected electric current is shown in Fig. 12, where curve
a shows those determined by an apparatus for detecting a
fuel concentration using an anode with the membrane as
shown in Fig. 5. The electric current changes with
5 concentration C_m but the change in electric current is
small. That is, the detection sensitivity is poor.

Furthermore, the adhesion between the platinum
plate 517a and the membrane 517b (Fig. 5) is often
inadequate, and the anolyte tends to stay therebetween,
10 deteriorating the response to changes in the methanol
concentration. When a platinum-based catalyst layer is laid
on the platinum plate 517a in place of the membrane 517b,
much detected current can be obtained as shown by curve b
in Fig. 12, but there is no change in the detected current
15 in the practical range (about 0.3 - about 2 moles/l) and
such a structure cannot be used as a sensor.

Cyclic voltammetry using a reference electrode
and an apparatus for detecting a fuel concentration by means
of a small fuel cell as disclosed in Japanese Patent
20 Application Kokai (Laid-open) No. 56-118273 are also
available as another apparatus for detecting a fuel concent-
ration. In the case of the cyclic voltammetry, a reference
electrode is required in addition to the detecting
electrodes, and also a function generator and other devices
25 are required, complicating the detecting system and
deteriorating the reliability, the most important task of
the sensor.

In the case of the apparatus using a small fuel

1 cell, not only the apparatus is dipped in the anolyte tank,
but also an additional air supply system is required, and
there is a difficulty in reduction in the apparatus size
as well as in the reliability.

5 In the case of using methanol or formalin as
fuel rather than using hydrazine as fuel, the detected power
output changes in a complicated manner even according to
the cyclic voltammetry, and the determination is sometimes
difficult to make.

10 There is other procedure for supplying a fuel
when an integrated load current becomes constant, since the
fuel concentration is proportional to the load current, but
when the load is greatly changed or the operation of fuel
cell is subject to repetitions of discontinuation, the fuel
15 concentration will be greatly deviated and cannot be
practically determined. A gas concentration sensor based
on semi-conductors requires much time until it is settled
for the measurement, and thus the response becomes poor.

Thus, a liquid fuel cell with a reliable
20 apparatus for detecting a fuel concentration in a simple
structure is in keen demand.

SUMMARY OF THE INVENTION

An object of the present invention is to provide
a liquid fuel with an improved supply of fuel and water to
25 a fuel circulation system which can operate continuously
and stably for a prolonged time in spite of differences in
the consumption rates of fuel and water.

1 Another object of the present invention is to
provide a liquid fuel cell with an apparatus for detecting
a fuel concentration with a high reliability and a high
sensitivity in a simple structure.

5 The present invention provides a liquid fuel
cell having a circulation system for a fuel mixture
comprising fuel and water, which comprises a first tank
containing water or a water-rich fuel mixture comprising
water and fuel, a second tank containing fuel or a fuel-rich
10 mixture comprising water and fuel, a first detector for
detecting the liquid level of the fuel mixture in the
circulation system, a second detector for detecting a fuel
concentration of the fuel mixture in the circulation system,
or an output from the fuel cell, or a load current of the
15 fuel cell, a valve means for controlling flow of the water
or the water-rich mixture in the first tank to the
circulation system in accordance with the output from the
first detector, and a valve means for controlling flow of
the fuel or the fuel-rich mixture in the second tank to the
20 circulation system in accordance with the output from the
second detector.

 According to the present invention, an apparatus
for detecting a fuel concentration by electrochemical
reaction, comprising an anode electrode provided with a
25 fuel-controlling layer for controlling permeation of fuel
through a catalyst layer, a cathode electrode, a power
source and a detector, the anode electrode and the cathode
electrode being dipped in the fuel mixture and a voltage

1 being applied to the electrodes is used as a second
detector in the present liquid fuel cell.

Fuel cannot be too concentrated in the fuel
circulation system, because at a higher fuel concentration,
5 excess fuel is liable to permeate into the oxidizing agent
electrode from the fuel electrode through the electrolyte
chamber, and undergo direct oxidation, i.e. direct consump-
tion, considerably lowering the fuel utilization efficiency.
Usually the fuel concentration in the fuel circulation
10 system is about 0.3 to about 2 moles/l, and the absolute
amount of the fuel in the fuel circulation system is small.

Thus, in the present invention a fuel concentra-
tion sensor is used to detect the fuel concentration in the
fuel circulation system to supply the fuel, or an output
15 voltage or output current of the fuel cell is detected
because the output voltage or current is reduced as the fuel
concentration is lowered. When the detected value becomes
lower than the standard concentration, a signal to open the
valve to the fuel tank is emitted to supply the fuel to the
20 fuel circulation system.

A considerably large amount of water is present
in the fuel circulation system, and thus it is preferable
to supply the water to the fuel circulation system to
checking whether a predetermined amount of water is retained
25 in the fuel circulation system satisfactorily or not. To
this end, a liquid level sensor is provided in the fuel
circulation system of the fuel cell to detect whether the
liquid level becomes lower than the standard level or not.

1 When the liquid level is detected lower than the standard
level, a signal to open the valve to the water tank is
emitted to supply the water to the fuel circulation system.

In the present invention, two tanks, i.e. fuel
5 tank and water tank, are provided, and only fuel is stored
in the fuel tank and only water in the water tank. However,
it is more preferable and more advantageous for the
operation of the fuel cell to distribute the necessary
amounts of fuel and water to the individual tanks, that is,
10 to store mixtures of fuel and water in the individual tanks.
When only fuel is supplied to the fuel circulation system
from the fuel tank, higher fuel concentration is locally
and transiently developed in the fuel circulation system
owing to the restricted circulation rate, unpreferably
15 lowering the fuel utilization efficiency transiently. This
problem can be solved by storing a fuel-rich mixture of
fuel and water in the fuel tank. Preferable molar ratio
of water to fuel in the fuel-rich mixture is 5 - 0 : 1,
where zero means only fuel. It is preferable to select a
20 ratio approximating to the ratio of consumption rate of
water to that of fuel on average during the operation of
the fuel cell.

When only water is supplied to the fuel
circulation system from the water tank, lower fuel
25 concentration is likewise locally and transiently developed
in the fuel circulation system owing to the restricted
circulation rate, and the fuel becomes short locally,
unpreferably lowering the performance of the fuel cell.

1 The problem can be solved by storing a water-rich mixture
of fuel and water in the water tank. Preferable molar ratio
of fuel to water in the water-rich mixture is 1 to 0 : 1,
where zero means only water. It is preferable to select a
5 ratio approximating to the fuel concentration in the fuel
circulation system in the fuel cell.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view showing the principle
of a liquid fuel cell.

10 Fig. 2 is a schematic view showing the principle
of a fuel cell having a fuel circulation system according
to the prior art.

Fig. 3 is a characteristic diagram showing
relationship between the fuel concentration and the cell
15 voltage.

Fig. 4 is a schematic view showing a fuel cell
with an apparatus for detecting a fuel concentration
according to the prior art.

Fig. 5 is a schematic view of an apparatus for
20 detecting a fuel concentration according to the prior art.

Fig. 6 is a schematic view of a liquid fuel cell
according to one embodiment of the present invention.

Figs. 7 and 8 are schematic views showing liquid
fuel cells according to other embodiments of the present
25 invention.

Fig. 9 is a schematic view showing an apparatus
for detecting a fuel concentration according to one

1 embodiment of the present invention.

Figs. 10 and 11 are schematic views showing apparatuses for detecting a fuel concentration according to other embodiments of the present invention.

5 Fig. 12 is a characteristic diagram showing a relationship between the fuel concentration and the detected electric current.

PREFERRED EMBODIMENTS OF THE INVENTION

One embodiment of the present invention will be
10 described, referring to Fig. 6, where a liquid fuel cell using methanol as fuel and sulfuric acid as an electrolyte is illustrated. Electrodes 2 (fuel electrode 2-1 and oxidizing agent electrode 2-2) are each made from a porous carbon plate as a substrate and a catalyst of platinum-
15 based substance supported on carbon powders, the catalyst being deposited on the substrate. Through a fuel chamber 4, a liquid mixture of methanol and dilute sulfuric acid, which, of course, contains water, is circulated as an anolyte by a pump 9. A carbon dioxide gas is generated at
20 the fuel electrode 2-1 as a product gas 811.

Air is supplied to an oxidizing agent chamber 5 as an oxidizing agent 7, and the exhaust gas 82 contains formed water at the same time.

A liquid level sensor 12 is provided on the liquid
25 level corresponding to the liquid level threshold value near the upper end of the electrodes 2 in the fuel circulation system. When the liquid level is lowered, the sensor

1 12 works to emit a signal to open the valve 111 and
supply the necessary amount of water from the water tank
101 to the fuel circulation system.

A methanol concentration sensor 13 based on the
5 electrochemical reaction is provided in the fuel circulation
system and set to the methanol concentration of 1 mole/l.
When the methanol concentration in the fuel circulation
system becomes lower than the set value, the sensor 13 works
to emit a signal to open the valve 112 and supply the
10 necessary amount of the fuel from the fuel tank 102 to the
fuel circulation system. The valves may be pumps.

In a liquid fuel cell with the structure of Fig. 6
and with a power output of 12 V and 100 W, the circulation
rate of the anolyte in the fuel circulation system is set
15 to 700 cc/min., and about 30 cc of water is supplied to
the fuel circulation system from the water tank 101 with
one opening of the valve 111 by the signal from the liquid
level sensor 12 when the liquid level is lowered in the fuel
circulation system. About 10 cc of fuel is supplied to
20 the fuel circulation tank from the fuel tank 102 with one
opening of the valve 112 by the signal from the methanol
concentration sensor 13 when the fuel concentration becomes
lower than 1 mole/l.

The fuel concentration during the operation of
25 liquid fuel cell is not necessarily 1 mole/l, and operation
at a higher fuel concentration is possible, if the load
current is relatively large, whereas the operation at a
lower fuel concentration is also possible, if the load

1 current is relatively small.

To set a fuel concentration, the set electric current must be changed, because the electric current is a function of fuel concentration according to the constant
5 voltage system when the electrochemical reaction is utilized.

As described above, a liquid fuel cell with two tanks, i.e. a fuel tank containing only fuel and a water tank containing only water can be operated stably against
10 fluctuations in load current, operating temperature or atmosphere.

Another embodiment of the present invention will be described below, referring to Fig. 7, where, when the liquid level is detected lower by the liquid level sensor
15 in the same liquid fuel cell as in Fig. 6, a water-rich fuel mixture is supplied from the water tank 101 in place of only water. That is, since the fuel concentration in the fuel circulation system is 1 mole/l, the water-rich fuel mixture in the water tank 101 is made to have a methanol
20 concentration of 1 mole/l. That is, the molar ratio of methanol to water is about 0.02.

In place of measuring the fuel concentration in the fuel circulation system, such a phenomenon that the output voltage is lowered as the fuel concentration is
25 decreased can be also utilized. To this end, a detector 15 to check an output voltage level is provided as shown in Fig. 7, and when a decrease in the output voltage level is detected, the valve 112 to the fuel tank 102 is opened with

1 a signal from the detector 15 to supply the fuel to the
fuel circulation system. In that case, a fuel-rich mixture
of fuel and water is supplied from the fuel tank 102
in place of fuel only to suppress local and transient
5 increase in the fuel concentration in the fuel circulation
system. Molar ratio of water to methanol in the fuel-rich
mixture in the fuel tank 102 is 2. In this case, total
volume of the water and the fuel in both tanks is the same :
as in the embodiment of Fig. 6.

10 In this embodiment, both tanks 101 and 102 contain
fuel mixtures, and local and transient unbalance of fuel
concentration in the fuel circulation system can be largely
improved, and thus the circulation rate by pump 9 through
the fuel circulation system can be much reduced, and a
15 good fuel cell performance can be obtained even at the
reduced circulation rate of 200 cc/min.

Further embodiment of the present invention will
be shown in Fig. 8, where only differences from the embodi-
ment of Fig. 7 are that a signal for supplying a fuel-rich
20 mixture from the fuel tank 102 to the fuel circulation
system is emitted in accordance with a decrease in the load
current of a liquid fuel cell. A detector 16 is connected to
two end points of a resistor 18 at the fuel electrode 2-1
and the valve is opened with a signal from the detector 16,
25 and further that a portion or all of water contained in the
exhaust gas 82 from the oxidizing agent chamber 5 is
recovered in a trap 17 and returned to the tank 101. By
the provision of the water recovery trap, the capacity of

1 water tank 101 can be reduced.

In the foregoing embodiments, liquid fuel cells using methanol as fuel and an acidic electrolyte have been described, but the present invention is readily applicable
5 also to an alkaline type liquid fuel cell using methanol as fuel, and other liquid fuel cells using hydrazine, formaldehyde, etc. as fuel by providing the fuel cell with two tanks and selecting fuel-water ratios of fuel mixtures in the tanks, as described above.

10 When a apparatus for detecting a fuel concentration according to the following embodiments is used in the present liquid fuel cell, the effects of the present liquid fuel can be further improved as described below.

In Fig. 9, an apparatus 516 for detecting a fuel
15 concentration according to one embodiment of the present invention is schematically given, which comprises an anode 517, a cathode 518, a power source 519 and a detector 520, as in the prior art, but the anode 517 has a fuel-controlling layer 517b' through a catalyst layer 521 in the
20 present invention. The fuel-controlling layer 517b' is prepared from a carbon fiber paper treated with a suspension of fine polytetrafluoroethylene particles by baking to give a controlled permeation and a strong water repellency to the paper. The fuel permeation can be
25 adjusted to, for example, about 7×10^{-6} moles/cm².min.mole/l by the treatment. A platinum-based catalyst layer 521 is provided on one side of the layer 517b' by kneading the catalyst with the same suspension of fine polytetra-

1 fluoroethylene particles as used above and applying the
mixture to the one side of the layer 517b', followed by
baking, thereby bonding the catalyst layer to the fuel-
controlling layer. Then, the resulting integrated layers
5 are tightly laid on an anode plate 517a made from, for
example, tantalum to contact the catalyst layer with the
anode plate 517a. It is preferable to fix the anode
517 to a frame serving also as a support for the anode so
that the fuel can permeate from the fuel-controlling layer
10 side.

That is, resin coats or pad plates of bakelite
or glass are laid on all other sides than the fuel-
controlling layer by an adhesive resin to form a seal
layer (not shown in the drawings), thereby preventing all
15 the other sides from direct contact with the anolyte.

In a practical test of the apparatus of Fig. 9
under such conditions that the electrode area is 4 cm^2 ,
the voltage is 0.9 volts, the fuel permeation through the
fuel-controlling layer 517b' is 1×10^{-6} to 2×10^{-5}
20 $\text{mole/cm}^2 \cdot \text{min} \cdot \text{mole/l}$) and a fuel concentration is 0 to 1.5
moles/l, the detected current has a good linearity and
a good sensitivity, shown by curve C in Fig. 12. That is,
in the apparatus of Fig. 9, the catalyst layer 521 is
provided between the anode 517a and the fuel-controlling
25 layer 517b', and no liquid stagnation occurs therebetween,
improving the permeation of the liquid, detection sensitivity
and detection response.

The fuel-controlling layer 517b' for use in the

1 present invention is not only a fibrous carbon paper but
can be also a porous carbon sheet, or can be an electro-
conductive porous material such as sintered metal. In that
case, the fuel-controlling layer must have only a function
5 to control the permeation of fuel, and thus an insulating
sintered ceramics or organic porous materials can be also
used. To provide the catalyst layer on the fuel-controlling
layer, various other techniques such as coating, deposition,
electrophoresis, CVD, etc. can be also used.

10 In Fig. 10, another embodiment of the present
invention is shown, where the fuel-controlling layer is
used double. That is, a second fuel-controlling layer 517c
is provided on the fuel-controlling layer 517b' at the
cathode-facing side, where the second fuel-controlling
15 layer 517c is prepared from a kneaded mixture of carbon
powders or graphite fluoride powders with a suspension of
fine polytetrafluoroethylene particles having a water
repellency and an adhesiveness by applying the kneaded
mixture to the surface of fuel-controlling layer 517b',
20 followed by baking to integrate these two layers. Cathode
518 is prepared from a cathode plate 518a other than a
platinum plate and a catalyst layer 518b laid on the cathode
plate by deposition or by electrophoresis, and no special
material is required for the cathode plate 518a. That is,
25 a cathode with a good detection sensitivity can be obtained
at a low cost.

In Fig. 11, other embodiment of the present
invention is shown, where the cathode is improved by

1 preparing a cathode 518 by laying a catalyst layer 518b on
an electroconductive, porous material 518c and tightly
laying the integrated porous material 518c and catalyst
layer 518b on a cathode plate 518a. As an electroconductive
5 porous material, carbon fiber paper or electroconductive
polymer, sintered metal, etc. can be used to ensure the
tight adhesion between the cathode plate 518a and the
catalyst layer 518b.

According to the present invention, a liquid fuel
10 cell can be stably and efficiently operated for a prolonged
time in spite of different consumption rates of fuel and
water even if the load current or operating temperature of
the fuel cell or the temperature or humidity of the
atmosphere is changed.

15 Further, according to the present invention, an
anode electrode having a fuel-controlling layer deposited
thereon through a catalyst layer is used in the present
apparatus for detecting a fuel concentration, and thus no
liquid fuel stagnation occurs between the anode electrode
20 and the fuel-controlling layer, improving the permeation
of liquid fuel and activation of the reaction between the
electrodes as well as improving the detection sensitivity
and response and thus the reliability of the apparatus.

WHAT IS CLAIMED IS:

1. A liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank (101) containing water or a water-rich fuel mixture comprising water and fuel, a second tank (102) containing fuel or a fuel-rich mixture comprising water and fuel, a first detector (12) for detecting the liquid level of the fuel mixture in the circulation system, a second detector (13) for detecting a fuel concentration of the fuel mixture in the circulation system, or an output from the fuel cell, or a load current of the fuel cell, a valve means (111) for controlling flow of the water or the water-rich mixture in the first tank to the circulation system in accordance with the output from the first detector (12), and a valve means (112) for controlling flow of the fuel or the fuel-rich mixture in the second tank to the circulation system in accordance with the output from the second detector (13).
2. A liquid fuel cell according to claim 2, wherein the water-rich mixture in the first tank (101) is a mixture of water and fuel having a molar ratio of fuel to water of not more than 1, and the fuel-rich mixture in the second tank (102) is a mixture of water and fuel having a molar ratio of water to fuel of not more than 5.
3. A liquid fuel cell according to claim 1 or 2, wherein the fuel is methanol.

4. A liquid fuel cell according to claim 1, wherein means (17) for recovering water discharged from an oxidizing agent chamber of the fuel cell into the first tank are provided.

5. A liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank (101) containing water or a water-rich fuel mixture comprising water and fuel, a second tank (102) containing fuel or a fuel-rich mixture comprising water and fuel, a first detector (12) for detecting the liquid level of the fuel mixture in the circulation system, a second detector (13) for detecting a fuel concentration of the fuel mixture in the circulation system, a valve means (111) for controlling flow of the water or the water-rich mixture in the first tank (101) to the circulation system in accordance with the output from the first detector (12), and a valve means (112) for controlling flow of the fuel or the fuel-rich mixture in the second tank (102) to the circulation system in accordance with the output from the second detector (13), the second detector (13) being an apparatus for detecting a fuel concentration by electrochemical reaction and comprising an anode electrode (517) provided with a fuel-controlling layer (517b') for controlling permeation of fuel through a catalyst layer (521), a cathode electrode (518), a power source (519) and a detector (520), the anode electrode (517) and the cathode electrode (518)

being dipped in the fuel mixture and a voltage being applied to the electrode.

6. A liquid fuel cell according to claim 5, wherein the fuel is methanol.

7. A liquid fuel cell according to claim 5 or 6, wherein the water-rich mixture in the first tank (101) is a mixture of water and fuel having a molar ratio of fuel to water of not more than 1, and the fuel-rich mixture in the second tank (102) is a mixture of water and fuel having a molar ratio of water to fuel of not more than 5.

8. A liquid fuel cell according to claim 5, wherein means (17) for recovering water discharged from an oxidizing agent chamber of the fuel cell into the first tank are provided.

9. A liquid fuel cell according to claim 5, wherein the anode electrode has a second fuel-controlling layer (517c) on the fuel-controlling layer (517b').

10. A liquid fuel cell according to claim 5, wherein the cathode electrode comprises a cathode plate (518a) other than a platinum plate, and a catalyst layer (518b).

11. A liquid fuel cell according to claim 5, wherein the cathode electrode comprises a cathode plate (518a) other than a platinum plate, an electroconductive porous layer (518c) and a catalyst layer (518b).

FIG. 1 PRIOR ART

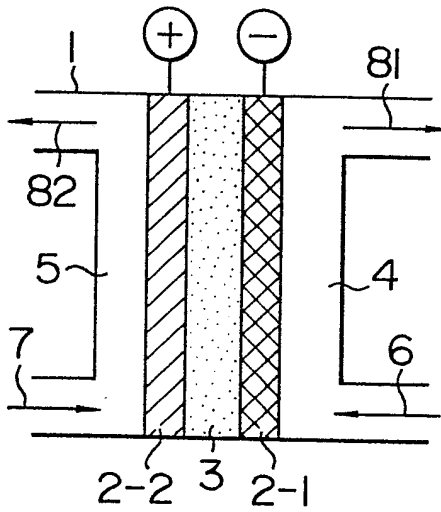


FIG. 2 PRIOR ART

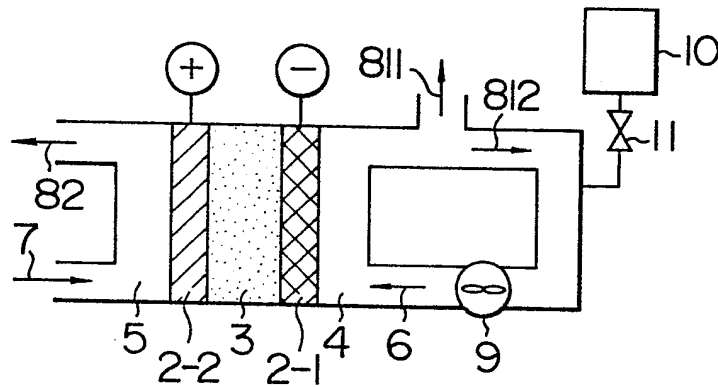


FIG. 3

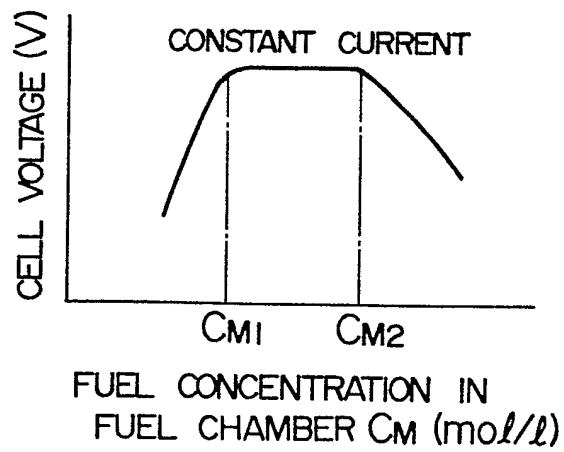


FIG. 6

The diagram shows a cross-section of an electrolyzer cell with a central cathode (3) and two side anodes (2-1 and 2-2). A hydrogen pump (9) is connected to the cathode side. The system includes a gas-liquid separator (12) and two storage tanks (101 and 102) for hydrogen and oxygen, respectively. The tanks are connected to the electrolyzer via valves (111 and 112) and a control unit (15) that receives signals from a positive (+) and negative (-) terminal. The electrolyzer is divided into three regions: 5 (left), 4 (middle), and 3 (right).

[illegible]

FIG. 9

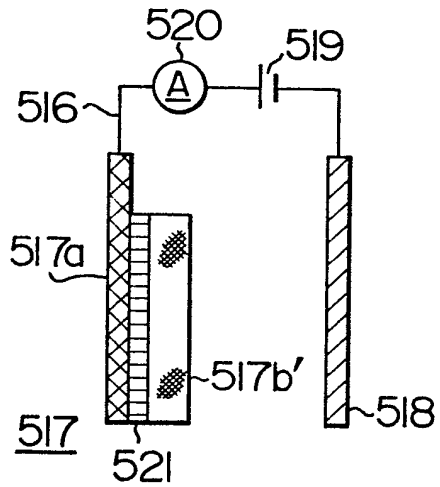


FIG. 10

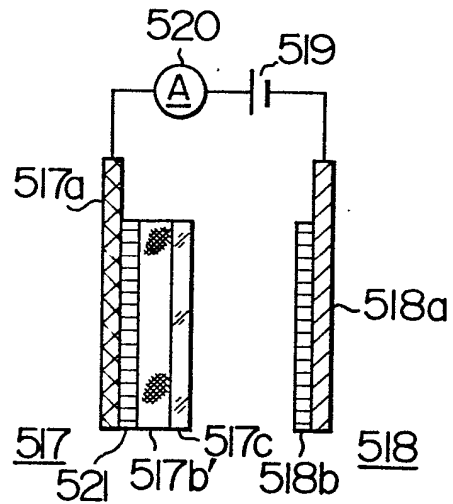
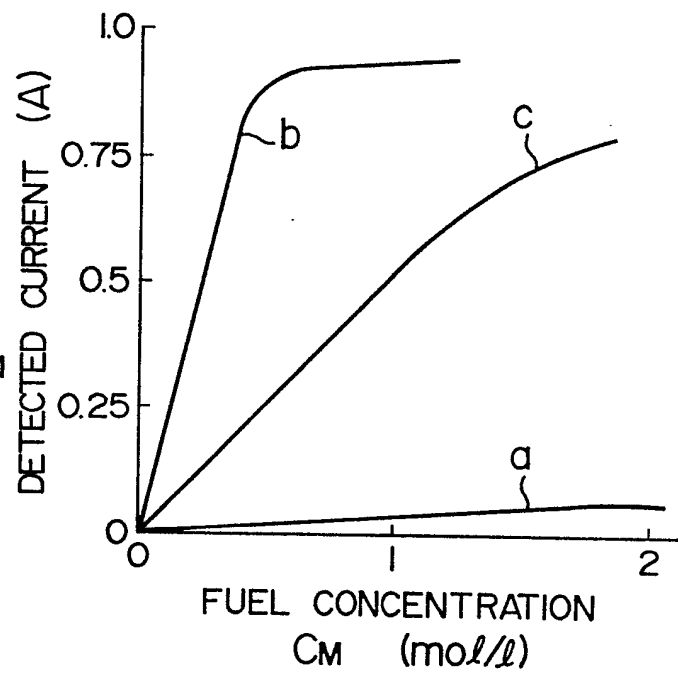
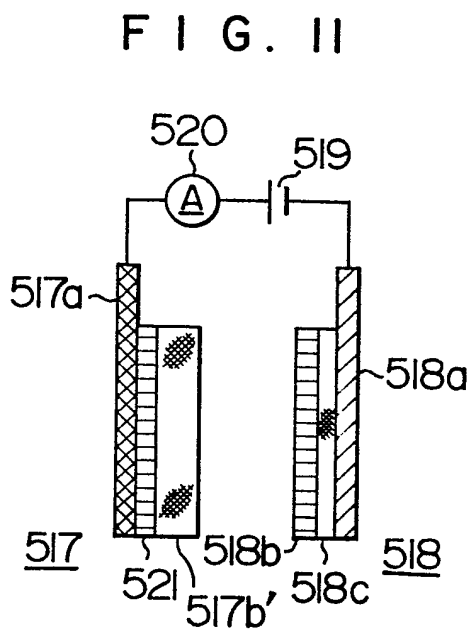


FIG. 12



12 **EUROPEAN PATENT APPLICATION**

21 Application number: **85113834.7**

51 Int. Cl.4: **H 01 M 8/04**

22 Date of filing: **30.10.85**

30 Priority: **31.10.84 JP 229277/84**
10.04.85 JP 74264/85

43 Date of publication of application: **21.05.86**
Bulletin 86/21

84 Designated Contracting States: **DE FR GB**

88 Date of deferred publication of search
report: **30.12.86 Bulletin 86/52**

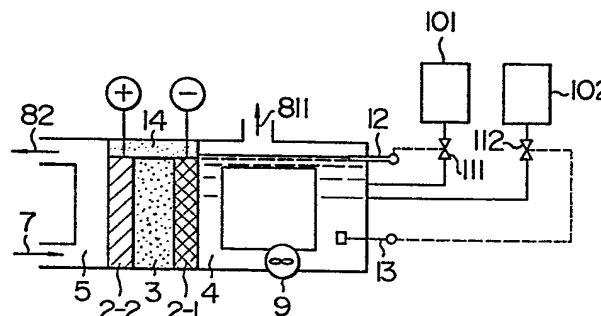
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64 **Liquid fuel cell.**

67 A liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank (101) containing water or a water-rich fuel mixture comprising water and fuel, a second tank (102) containing fuel or a fuel-rich mixture comprising water and fuel, a first detector (12) for detecting the liquid level of the fuel mixture in the circulation system, a second detector (13) for detecting a fuel concentration of the fuel mixture in the circulation system, or an output from the fuel cell, or a load current of the fuel cell, a valve means (111) for controlling flow of the water or the water-rich mixture in the first tank to the circulation system in accordance with the output from the first detector (12), and a valve means (112) for controlling flow of the fuel or the fuel-rich mixture in the second tank (102) to the circulation system in accordance with the output from the second detector (13). The liquid fuel cell can be stably and efficiently operated for a prolonged time in spite of different consumption rates of fuel and water even if the load current or operating temperature of the fuel cell or the temperature or humidity of the atmosphere is changed.





European Patent
Office

EUROPEAN SEARCH REPORT

0181569

Application number

EP 85 11 3834

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 288 (E-218)[1433], 22nd December 1983; & JP-A-58 165 274 (HITACHI SEISAKUSHO K.K.) 30-09-1983 * Whole abstract * ---	1,3-5	H 01 M 8/04
Y	EP-A-0 072 038 (HITACHI) * Claims 1,4,5,7,8; figure 3; page 6, lines 5-7 * ---	1,3-5	
Y	DE-A-1 812 870 (SIEMENS AG) * Claims 1,3,9; page 2, lines 26-28 * ---	1,3-5	
A	US-A-3 542 597 (J.O. SMITH et al.) * Figure 2; column 4, line 71 - column 5, line 12; column 6, lines 25-56,69-73; claim 1 * ---	1	
A	PATENTS ABSTRACTS OF JAPAN, vol. 8, no. 268 (E-283)[1705], 7th December 1984; & JP-A-59 138 074 (HITACHI SEISAKUSHO K.K.) 08-08-1984 * Whole abstract * -----	2	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-10-1986	Examiner D' HONDT J.W.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	